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SPECIFICATION

1. Title of the invention

A method for the production of epichlorohydrin

2. Scope of the Patent Claims

A method for the production of epichlorohydrin, characterized in that, when producing epichlorohydrin by means of a dehydrochlorination reaction using an alkali aqueous solution or alkali liquid suspension which contains from 1 to 1.2 mol equivalent of alkali per mol equivalent of 2,3-dichloro-1-propanol and/or 1,3-dichloro-2-propanol, from 0.05 to 0.4 mol equivalent of the alkali is pre-mixed with the abovementioned dichloropropanol at from 10 to 40°C and partial dehydrochlorination is carried out and then the material is supplied continuously to a reaction-distillation column, together with from 1.15 to 0.7 mol equivalent of the alkali, and a dehydrochlorination reaction of the remaining part is carried out and the epichlorohydrin which is produced is stripped with steam and discharged from the column top.

3. Detailed Description of the Invention

Industrial Field of Application

The invention concerns a method with which epichlorohydrin is produced by the dehydrochlorination of 2,3-dichloro-1-propanol and/or 1,3-dichloro-2-propanol using an alkali.

Prior Art

Epichlorohydrin is used in large quantities as a raw material for epoxy resins and synthetic rubbers, as a stabilizer for chlorinated rubbers and as an intermediate or starting material for glycidyl ethers, glycidyl esters, glycerine and derivatives thereof and amine adducts and the like.

Conventionally, epichlorohydrin is produced industrially by mixing a liquid suspension of an alkali such as a calcium hydroxide with an aqueous solution of a low concentration of some 3 to 5 wt% of a mixture of 2,3-dichloro-1-propanol and 1,3-dichloro-2-propanol which has been obtained by reacting chlorine water with

allyl chloride and supplying the mixture to a plate type reaction-distillation column and carrying out dehydrochlorination and stripping with steam to discharge the epichlorohydrin which has been produced from the top of the column. The dichloropropanol which is obtained with this method is maintained in the range where it has adequate solubility in the liquid phase in the column in order to obtain an aqueous solution of low concentration as indicated above and no fall in the reaction rate is observed. On the other hand, a large quantity of steam is required for stripping off the product.

A method in which a high concentration of dichloropropanol such that it accounts for from 10 to 50 wt% of the total weight of the liquid being supplied to the reaction-distillation column has been proposed for achieving an improvement in terms of the amount of steam which is used (Japanese Unexamined Patent Application Laid Open 60-258172). However, when such a high concentration of dichloropropanol is used it has been confirmed that the apparent reaction rate is reduced when compared with that in the case where a dilute solution as aforementioned is used. That is to say, it has become possible recently to have a dichloropropanol concentration in the liquid which is being supplied excluding the alkali in the high region of from 50 to 80 wt% but the solubility of dichloropropanol in water is less than 20% in an aqueous solution at 60°C and less than 30% at 80°C and it is further reduced by the salting-out effect due to the salt which is produced during the reaction. Furthermore, the partition ratio of dichloropropanol in epichlorohydrin which is the product and water is about 10 : 1. Hence, a lowering of the dichloropropanol concentration in the aqueous alkali and a lowering of the apparent dehydrochlorination rate can be anticipated.

As the reaction rate falls so the dichloropropanol content of the distillate from the column top

increases. If the residence time in the column is prolonged then the conversion of the dichloropropanol is increased but the epichlorohydrin selectivity is reduced because of losses due to successive reactions. The dichloropropanol which has distilled off can be distilled and isolated and recycled but if a large amount is to be recycled then the amount of material being treated in the distillation column is increased and the plant cost and the energy cost are both increased and there is a further problem in that the amount of material lost is also increased and this is undesirable.

A method in which some of the alkali is supplied above the position at which the dichloropropanol is being supplied has been proposed as a means of resolving these problems (Japanese Unexamined Patent Application Laid Open 63-17874). In this method the chance of contact with the alkali again in the process where the epichlorohydrin which had been produced is being stripped with steam is increased and so stripping while avoiding the ring-opening reaction of the epichlorohydrin is accompanied by major problems in terms of both the design of the column and the stable operating conditions.

The present applicant has already proposed a method in which, when supplying dichloropropanol and aqueous alkali solution or an alkali liquid suspension to a plate type reaction-distillation column and producing epichlorohydrin, the part which is rich in dichloropropanol of the distillate at the column top is condensed using a partial condenser and, by refluxing this to the distillation column, even if the concentration of dichloropropanol in the liquid which is being supplied is high, it is possible to obtain epichlorohydrin in high yield with a high dichloropropanol conversion (Japanese Patent Application H1-281419). However, the fall in the apparent reaction rate which is caused by the raised concentration of dichloropropanol is not avoided and

compensation by operational control of just the partial condenser is certainly not simple.

Problems to be Resolved by the Invention

The purpose of the present invention is to provide a method with which, when supplying a high concentration of dichloropropanol together with an alkali aqueous solution or an alkali liquid suspension to a reaction-distillation column, the conversion of the dichloropropanol and the epichlorohydrin selectivity are both high.

Means of Resolving These Problems and Action

The inventors have discovered a method in which, when supplying dichloropropanol comprising 2,3-dichlo-1-propanol and/or 1,3-dichloro-2-propanol to the reaction-distillation column, the concentration of dichloropropanol in the mixture is reduced by means of a preliminary treatment at low temperature with an amount of alkali fraction which does not reach the mol equivalent of said dichloropropanol, and the fall in the apparent reaction rate which arises in cases where a high concentration dichloropropanol solution is used is corrected and epichlorohydrin can be obtained in high yield with a high dichloropropanol conversion, and the invention is based upon this discovery.

That is to say, the present invention is a method for the production of epichlorohydrin which is characterized in that, when producing epichlorohydrin by means of a dehydrochlorination reaction using an alkali aqueous solution or an alkali liquid suspension which contains from 1 to 1.2 mol equivalent of alkali per mol equivalent of 2,3-dichloro-1-propanol and/or 1,3-dichloro-2-propanol, from 0.05 to 0.4 mol equivalent of alkali is pre-mixed with the abovementioned dichloropropanol at from 10 to 40°C and partial dehydrochlorination is carried out and then the material is supplied continuously to a reaction-distillation column, together with from 1.15 to 0.7 mol equivalent of alkali, and a dehydrochlorination reaction of the remaining part is carried out and the

epichlorohydrin which is produced is stripped with steam and discharged from the column top.

The dichloropropanol which is used in this invention may be, as indicated above, 2,3-dichloro-1-propanol, 1,3-dichloro-2-propanol or a mixture of these.

The alkaline compounds which can be used for the dehydrochlorination reaction are hydroxides, oxides or weak-acid salts of the alkali metals or alkaline earth metals and, for example, sodium hydroxide, calcium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, calcium oxide, barium oxide or the like can be used in the form of an aqueous solution or liquid suspension. The amount used is from 1.0 to 1.2 times the theoretical amount required for the dehydrochlorination reaction of the dichloropropanol. The concentration of the alkali aqueous solution or liquid suspension which is used is suitably from 3 to 15 wt% in view of the ease of handling and the solubility of the dichloropropanol.

Before being supplied to the reaction-distillation column, the dicyclopropanol is subjected to a preliminary reaction in which it is treated at from 10 to 40°C with an alkali aqueous solution or alkali liquid suspension which contains from 0.05 to 0.3 mol equivalent of alkali from among the prescribed amount of alkali per 1 mol equivalent of dicyclopropanol and partially dehydrochlorinated.

The crude dichloropropanol product introduced from the earlier process can be dehydrochlorinated as it is without refinement by means of the method of this invention. The crude product often contains hydrogen chloride and so alkali is required for neutralization purposes. In this case the sum total of the abovementioned alkali fraction and the alkali fraction required for neutralization should be supplied at the time of the preliminary reaction. Even in those cases where such dichloropropanol which contains hydrogen chloride is used, the hydrogen chloride concentration

in the raw material feed port of the reaction-distillation column can be set to essentially zero if a preliminary reaction is carried out in accordance with the present invention and this has the effect of avoiding the neutralizing effect and destabilization of the dehydrochlorination reaction in the column and preventing corrosion of the column as a result of the presence of acid.

The dichloropropanol which had been subjected to the preliminary reaction is supplied to the reaction-distillation column at the prescribed flow rate. The alkali fraction remaining after some has been used in the preliminary reaction is mixed with the abovementioned dichloropropanol immediately before entering the feed port to the column and the mixture can be introduced through a single feed port, but in order to control more rigorously the conversion of the dichloropropanol in the preliminary reaction, fix the composition of the mixture and stabilize the reaction in the reaction-distillation column more rapidly and maintain a steady state, the supply from separate feed ports established at the same level in column is preferred. Alternatively, the alkali fraction may be supplied as a mixture with the liquid condensate of the partial condenser. When the epichlorohydrin which has been produced in the preliminary reaction is supplied to the column it is readily transferred into the vapour phase and the concentration of dichloropropanol in the liquid phase is low when compared with that when the preliminary reaction has not been carried out and so the apparent fall in the reaction rate which is caused by the solution concentration is suppressed. Moreover, by pre-raising the conversion of dichloropropanol by means of a preliminary reaction the residence time in the column can be shortened and the number of plates of the column can be reduced. The alkali concentration in the column can also be reduced and the formation of by-products is reduced and so the epichlorohydrin selectivity can also be raised. Furthermore, in the

case of industrial production the height of the column can be reduced and so there is a reducing effect on the plant cost including the mounting structure and other supplementary facilities. The mol equivalent ratio of dichloropropanol and alkali fraction and the temperature are important at the time of the preliminary reaction for obtaining effects such as these. In those cases where the alkali fraction is less than 0.05 mol equivalent per mol equivalent of dichloropropanol hardly any improving effect is obtained, and this is the same as the reaction where the material is supplied directly to the column without carrying out a preliminary reaction. Furthermore, in those cases where the alkali fraction is greater than 0.3 mol equivalent the dichloropropanol conversion is increased and the amount of by-product formation is also increased and so the epichlorohydrin selectivity is reduced and the loss of epichlorohydrin can no longer be neglected, and the effect of the preliminary reaction is not obtained and the reaction is of no significance. In those cases where the temperature of the preliminary reaction exceeds 40°C the loss due to hydrolysis of the epichlorohydrin which has been produced and the loss due to the addition reaction with the salt which has been produced are promoted and the epichlorohydrin selectivity after the whole of the reaction has been completed is inevitably reduced. In those cases where the temperature of the preliminary reaction is less than 10°C the reaction rate falls and the solubility of the dichloropropanol in the aqueous alkali is reduced and the preliminary reaction is unlikely to be completed within a practical period of time and, depending on the particular case, problems such as the composition of the feed into the column becoming unstable may arise, and this is undesirable.

A stirred-tank type reactor or tube-like reactor can be used as the apparatus for the preliminary reaction which is used in the invention. In the case of a tube-like reactor a part of the reactor may be in

the form of a loop so that the reaction mixture can be circulated and the mixing efficiency can be raised by circulating the liquid with a pump. A static mixer can be introduced into the circulating path and the mixing efficiency can be heightened even more. Furthermore, the preliminary reaction may be carried out in a continuous system or in a batch system.

The reaction-distillation column which is used in the method of the present invention may be a packed column, a perforated plate column, a downcomer fitted perforated plate column or such like column, but a perforated plate column with downcomer is especially desirable. For example, a column which has a feed port for the refluxed liquid at the uppermost stage of the column, a feed port for the raw material dichloropropanol and alkali fraction at a stage from four to six stages below the uppermost stage and a steam blow-in nozzle below the lowermost stage can be used.

When a dichloropropanol conversion and an epichlorohydrin selectivity of 90% or more are to be obtained the number of theoretical plates required is generally from thirteen to seventeen in those cases where the preliminary reaction of this invention has not been carried out, but ten or eleven theoretical plates is sufficient with the method of this present invention.

Illustrative Examples

The method for the production of epichlorohydrin of this invention is described in more practical terms below by means of illustrative examples. Moreover, the composition % values in the examples are all in units by weight, and the conversion and selectivity are as follows:

Conversion =

$$\left(1 - \frac{\text{No. of Mol of Dichloropropanol in the Liquid Distillate}}{\text{No. of Mol of Dichloropropanol Supplied}}\right) \times 100$$

Selectivity =

$$\frac{\dfrac{\text{No. of Mol of (Epichlorohydrin) Distilled Out}}{\text{No. of Mol of (Dichloropropanol) Supplied}} \times 100}{\text{Conversion}} \times 100$$

The reaction-distillation column was produced in such a way that it was easily taken apart and assembled for experimental purposes. The column itself comprised single units comprising steel cylinders of internal diameter 100 mm with flanges fitted to both ends with two downcomer-fitted perforated plates (open fraction 13%) of depth 15 mm per unit and the number of these units was increased or decreased in accordance with the number of plates required, and after assembly the distance between the plates was 150 mm. The feed port for the raw material and alkali fraction was established on the fifth plate and the steam blow-in nozzle was established below the lowermost plate. The discharge port at the column top was connected to a tubular type total condenser of heat-transfer area 0.3 m^2 via a tubular type partial condenser of heat-transfer area 0.3 m^2. The liquid condensate of the partial condenser was piped in such a way that it entered at the same stage as the raw material feed port and the liquid condensate of the total condenser was piped in such a way that it entered a liquid separating tank. The upper layer (aqueous layer) of liquid separating tank was piped in such a way that it was refluxed to the uppermost plate of the column and the

lower layer (oil layer) was piped into the distillate liquid receiver. Liquid was removed from the column bottom in such a way that the liquid surface level was held constant by means of a liquid-surface controller. The total condenser outlet port and the upper part of the liquid separating tank were connected to a vacuum pump so that the operating pressure of the column could be varied.

Example 1

Preliminary Reaction:

5.9 kg of water and a liquid suspension (18.3 kg) containing 5% calcium hydroxide were each pre-heated to about 40°C and then introduced into a stirred tank of capacity 50 l which was made of steel and jacketed and the liquid mixture was subjected to a 25 minute preliminary reaction at 40°C and then cooled immediately and stored at a temperature not exceeding 10°C. The preliminary reaction rate was 23%.

Reaction-distillation:

The liquid after the preliminary reaction was taken out from the bottom discharge port of the abovementioned stirred tank, with stirring, at a rate of 2.54 kg/hr and, together with 4.86 kg/hr of an alkali liquid suspension of the same concentration as above, supplied to the abovementioned reaction-distillation column. The reaction-distillation column had twenty four plates, steam was blown in from the steam blow-in nozzle at a rate of 1.7 kg/hr, and the column was operated for 8 hours at a column top pressure of 500 mmHg, a column top temperature of 86°C, a column bottom temperature of 99°C and a partial condenser temperature of 82°C and the system was stabilized. The partial condensation rate was about 40% with respect to the column top distillate. After the column had stabilized, the oil layer which had separated from the liquid condensate of the total condenser was sampled and analysed using gas chromatography and the 2,3-dichloro-1-propanol conversion was 98.0%, the epichlorohydrin selectivity

was 98.5% and the 2,3-dichloro-1-propanol content of the oil layer was 3.9%.

Example 2

Preliminary Reaction:

A 60 minute preliminary reaction was carried out in the same way as in Example 1 using 17.6 kg of a mixture of 58.5% 2,3-dichloro-1-propanol, 4.4% 1,3-dichloro-2-propanol, 26.9% water and 10.2% hydrogen chloride and 31.0 kg of a liquid suspension which contained 10% calcium hydroxide. The preliminary reaction rate was 40%.

Reaction-distillation:

In the same way as in Example 1, 4.86 kg/hr of the liquid which had been subjected to the preliminary reaction and 2.54 kg/hr of alkali liquid suspension of the same concentration as above were supplied to the same reaction-distillation column as used in Example 1 and the column was run for 8 hours while blowing in 1.7 kg/hr of steam from the steam blow-in nozzle at a column top pressure of 500 mmHg, a column top temperature of 85°C, a column bottom temperature of 99°C and a partial condenser temperature of 80°C, and the system was stabilized. The partial condensation rate was 50% with respect to the column top distillate. After the column had stabilized, the product was analysed in the same way as in Example 1 and the conversion of 2,3-dichloro-1-propanol and 1,3-dichloro-2-propanol combined was 99.2%, the epichlorohydrin selectivity was 98.3%, and the contents of 2,3-dichloro-1-propanol and 1,3-dichloro-2-propanol in the oil layer were 1.1% and 0.1% respectively.

Comparative Example

Without carrying out the preliminary reaction in Example 1, the 2,3-dichloro-1-propanol, water and liquid calcium hydroxide suspension were supplied directly to the abovementioned reaction-distillation column and a dehydrochlorination reaction was carried out in the same way as in Example 1. The 2,3-dichloro-

1-propanol conversion was 96.1%, the epichlorohydrin selectivity was 97.5% and the 2,3-dichloro-1-propanol content of the oil layer was 4.3%.

It is clear from the examples and comparative example described above that the dichloropropanol conversion and the epichlorohydrin selectivity in particular are improved by carrying out the preliminary reaction.

Effect of the Invention

By supplying the mixture to the reaction-distillation column after carrying out a preliminary reaction of the dichloropropanol with a small amount of the alkali at low temperature in accordance with the method of this invention it is possible to suppress the unwanted side reactions to the lowest limit. In this way, the alkali fraction which should be supplied to the column can be reduced and the alkali concentration in the column as a whole can be reduced, and hydrolysis of the epichlorohydrin can be reduced. These factors all raise the dichloropropanol conversion and at the same time have the effect of raising the epichlorohydrin selectivity. When a high concentration of dichloropropanol is used the apparent reaction rate of 2,3-dichloro-1-propanol in particular is markedly reduced and so the method of this invention is effective as a method of compensating for this reduction. Furthermore, in those cases where a mixture of 2,3-dichloro-1-propanol and 1,3-dichloro-2-propanol is used the reaction rate of the latter is greater and so the latter is consumed first by carrying out the preliminary reaction and when the mixture is supplied to the column the content of the former raw material is relatively increased and so the optimum or near-optimum operating conditions for the former raw material can be selected in the column and control of the reaction is facilitated. Moreover, the number of plates in the column can be reduced and progress of the reaction and by-product formation can be reduced when compared with that in the case where the whole of the reaction takes

place in the column and the organic content of the still bottom liquid is also reduced, for example, and so the method is useful industrially.

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PATENT ABSTRACTS OF JAPAN

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(54) PREPARATION OF EPICHLOROHYDRIN

(57)Abstract:
PURPOSE: To prepare epichlorohydrin in high conversion and yield by preliminarily reacting dichloropropanol with an alkali, feeding the preliminary reaction product into a reaction distillation tower and subsequently subjecting the product to the remaining dehydrochlorination reaction in the tower.
CONSTITUTION: 2,3-Dichloro-1-propanol and/or 1,3-dichloro-2-propanol is preliminarily treated with an aqueous solution or suspension containing 0.05-0.4 molar equivalent of an alkali (e.g. CaOH) at 10-40°C. The preliminarily treated product is continuously fed into a reaction distillation tower together with 1.15-0.7mol equivalent of an alkali for the remaining dehydrochlorination reaction to provide the objective compound. The epichlorohydrin is useful as a raw material for epoxy resins or synthetic rubbers, as a stabilizer for chlorinated rubbers, or as an intermediate or starting substance for glycidyl ethers, amine adducts or others.

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㊹発明の名称　エピクロルヒドリンの製造方法

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明　細　書

1.発明の名称

エピクロルヒドリンの製造方法

2.特許請求の範囲

2,3−ジクロロ−1−プロパノール及び／又は1,3−ジクロロ−2−プロパノールの1モル当量と1〜1.2モル当量のアルカリ分を含有するアルカリ水溶液又はアルカリ懸濁液とを用いて脱塩化水素反応によりエピクロルヒドリンを製造するに際し、予め上記ジクロロプロパノールに0.05〜0.4モル当量のアルカリ分を10〜40℃で混合して一部脱塩化水素させた後、1.15〜0.7モル当量のアルカリ分と共に反応蒸留塔に連続的に供給して残部を脱塩化水素させ、生成したエピクロルヒドリンを水蒸気によりストリッピングして塔頂から抜き出すことを特徴とするエピクロルヒドリンの製造方法。

3.発明の詳細な説明

〔産業上の利用分野〕

本発明は2,3−ジクロロ−1−プロパノール及び／又は1,3−ジクロロ−2−プロパノールをアルカリを用いて脱塩化水素してエピクロルヒドリンを製造する方法に関するものである。

〔従来の技術〕

エピクロルヒドリンはエポキシ樹脂や合成ゴムの原料，塩素化ゴムの安定剤，グリシジルエーテル類，グリシジルエステル類，グリセリン及びその誘導体，アミン付加物その他の中間体あるいは出発物質として多量に使用されている。

エピクロルヒドリンは、従来塩化アリルと塩素水との反応によって得られる2,3−ジクロロ−1−プロパノールと1,3−ジクロロ−2−プロパノールの混合物である3〜5重量%程度の低濃度水溶液を水酸化カルシウムのようなアルカリの懸濁液とを混合し、棚段式反応蒸留塔に供給して、脱塩化水素しつつ水蒸気でストリッピングさせ、塔頂から生成したエピクロルヒドリンを抜き出す方法で工業的に製造されている。この方法で得られるジクロロプロパノールは上記のように低濃度の水溶液として得られるため、塔内液相では十分な

溶解度の範囲内に保たれ、反応速度の低下は認められない。一方生成物のストリッピングのための水蒸気が多量に必要となる。

水蒸気の原単位をよくするために反応蒸留塔への供給液の合計重量に対して10～50重量%のような高濃度のジクロロプロパノールを使用する方法が提案されている（特開昭60－258172号）。しかしながらこのような高濃度のジクロロプロパノールを使用すると、前記のような希薄溶液を用いた場合に比べて見掛けの反応速度が低下することが判明した。すなわちアルカリ分を除いた供給液中のジクロロプロパノール濃度が50～80重量%のような高濃度のものが最近入手可能となったが、ジクロロプロパノールの水への溶解度は水溶液中60℃で20%以下、80℃で30%以下であり、反応中生成する塩による塩析効果でさらに低下する。また生成物であるエピクロルヒドリンと水へのジクロロプロパノールの分配比はほぼ10：1である。したがってアルカリ水中のジクロロプロパノール濃度が低くなり、見掛けの脱塩化水素速度が低下するものと推察される。

反応速度の低下に伴い、塔頂留出物中のジクロロプロパノールが増加する。塔内の滞留時間を長くすればジクロロプロパノールの転化率は上昇するが、逐次反応による消費のために、エピクロルヒドリンの選択率が低下する。留出したジクロロプロパノールを蒸留で分離してリサイクルすることも可能であるが、リサイクルすべき量が多いと蒸留塔での処理量が増え、設備費，エネルギーコスト共に増大し、損失量も増える等弊害が出て好ましくない。

これらの問題点を解決する方法としてアルカリ分の一部をジクロロプロパノールの供給位置より上部に供給する方法が提案されている（特開昭63－17874号）。この方法では生成したエピクロルヒドリンが水蒸気によりストリッピングされる過程で再びアルカリ分と接触する機会が増えるため、エピクロルヒドリンの開環反応を防ぎながらストリッピングすることは、塔の設計及び安定操作条件の両面から大きな困難を伴う。

本出願人は先に、棚段式反応蒸留塔にジクロロプロパノールとアルカリ水溶液もしくはアルカリ懸濁液とを供給してエピクロルヒドリンを製造するに際し、分縮器を用いて、塔頂留出物のジクロロプロパノールに富む部分を凝縮させて蒸留塔に還流させることにより、供給液中のジクロロプロパノールの濃度が高い場合でも、ジクロロプロパノールの高い転化率でエピクロルヒドリンを高収率で得ることができる方法を提案した（特願平1－281419）。しかしながら、上記のように、ジクロロプロパノールの高濃度化に起因する見掛けの反応速度の低下は避けられず、これを分縮器のみの運転制御によって補うことは必ずしも容易ではない。

〔発明が解決しようとする課題〕

本発明の目的は、高濃度のジクロロプロパノールをアルカリ水溶液又はアルカリ懸濁液と共に反応蒸留塔に供給する際のジクロロプロパノールの転化率及びエピクロルヒドリンの選択率を共に高くする方法を提供することにある。

〔課題を解決するための手段及び作用〕

本発明者らは、2,3－ジクロロ－1－プロパノール及び／又は1,3－ジクロロ－2－プロパノールからなるジクロロプロパノールを反応蒸留塔に供給するに際して、該ジクロロプロパノールのモル当量に達しない量のアルカリ分で、かつ低温で予め処理することにより、混合物中のジクロロプロパノールの濃度を低下させ、高濃度のジクロロプロパノール溶液を用いた場合に生じる見掛けの反応速度の低下を補い、ジクロロプロパノールの高い転化率でエピクロルヒドリンを高収率で得る方法を見出し、本発明を完成した。

すなわち本発明は、2,3－ジクロロ－1－プロパノール及び／又は1,3－ジクロロ－2－プロパノールの1モル当量と1～1.2モル当量のアルカリ分を含有するアルカリ水溶液又は懸濁液を用いて脱塩化水素反応によりエピクロルヒドリンを製造するに際し、予め上記ジクロロプロパノールに0.05～0.4モル当量のアルカリ分を10～40

てで混合して一部脱塩化水素させた後、1.15～0.7モル当量のアルカリ分と共に反応蒸留塔に連続的に供給して残部を脱塩化水素させ生成したエピクロルヒドリンを水蒸気によりストリッピングして塔頂から抜き出すことを特徴とするエピクロルヒドリンの製造方法である。

本発明で用いられるジクロロプロパノールは上記のように2,3－ジクロロ－1－プロパノールでもよいし、1,3－ジクロロ－2－プロパノールでもよく、これらの混合物でもよい。

脱塩化水素反応に用いるアルカリ性化合物としてはアルカリ金属又はアルカリ土類金属の水酸化物，酸化物、又は弱酸との塩であり、例えば水酸化ナトリウム，水酸化カルシウム，水酸化カリウム，炭酸ナトリウム，炭酸カリウム，酸化カルシウム，酸化バリウム等を水溶液又は懸濁液として使用する。その使用量はジクロロプロパノールの脱塩化水素反応に要する理論量の1.0～1.2倍である。ここに用いるアルカリ水溶液又は懸濁液の濃度は取扱いやすさ，ジクロロプロパノールの溶解度から3～15重量%が適当である。

ジクロロプロパノールは反応蒸留塔に供給する前に、その1モル当量に対して、所定量のアルカリ分のうち0.05～0.3モル当量のアルカリ分を含有するアルカリ水溶液又はアルカリ懸濁液と10～40℃で処理して一部脱塩化水素させる予備反応を行う。

ジクロロプロパノールとして、前工程から導かれる粗製品を精製することなく、そのまま本発明の方法により脱塩化水素させることができる。粗製品はしばしば塩化水素を含有しているので、中和のためのアルカリが必要である。この場合は予備反応に際して、上記のアルカリ分と中和に要するアルカリ分との合計量を供給すればよい。このように塩化水素を含有するジクロロプロパノールを用いる場合でも、本発明による予備反応を実施すれば反応蒸留塔の原料フィード口においては、塩化水素濃度を実質的にゼロにすることができ、塔内での中和反応と脱塩化水素反応の非定常化の防止，酸の存在による塔の腐食の防止等に効果がある。

予備反応したジクロロプロパノールは、所定の流量で反応蒸留塔に供給する。予備反応に用いた分の残りのアルカリ分は上記ジクロロプロパノールと塔へのフィード口の直前で混合して1つのフィード口から供給してもよいが、予備反応におけるジクロロプロパノールの転化率を厳密に制御し、混合物の組成を一定にして、反応蒸留塔内の反応を速やかに安定化させて定常状態を保持するためには、塔の同じ段に設けた別のフィード口から供給するのが望ましい。あるいはこのアルカリ分は分縮器の凝縮液と混合して供給してもよい。予備反応で生成したエピクロルヒドリンは塔に供給されると、容易に気相に移行し、液相中のジクロロプロパノールの濃度は、予備反応を行わなかったときと比較して低くなるのでその分溶解度に起因する反応速度の見掛けの低下は押えられる。さらに予備反応によってジクロロプロパノールの転化率を予め上げておくことにより、塔内の滞留時間を短くすることができ、塔の段数を少くすることも可能となる。塔内でのアルカリ濃度もその分低くできることとも相俟って副生物の生成を軽減してエピクロルヒドリンの選択率を高くすることができる。また工業的生産に際しては塔の高さを低くすることができるから、架構その他の付帯設備も含めてプラントコストの低減に効果がある。このような効果を得るために、予備反応に際しては、ジクロロプロパノールとアルカリ分のモル当量比及び温度が重要である。ジクロロプロパノールの1モル当量に対して、アルカリ分が0.05モル当量未満の場合は殆ど改善効果が得られず、予備反応を行わず直ちに塔へ供給して反応させた場合と同等である。またアルカリ分が0.3モル当量を超える場合はジクロロプロパノールの転化率が高くなると共に副生物の生成量が増えることによりエピクロルヒドリンの選択率が低下してエピクロルヒドリンの損失が無視できなくなり、予備反応の効果が得られず無意味である。予備反応の温度が40℃を超える場合はやはり生成したエピクロルヒドリンの加水分解による消費及び生成した塩と

の付加反応による消費が促進され、全反応終了後のエピクロルヒドリンの選択率が低下してしまう。予備反応の温度が10℃未満の場合は反応速度の低下、ジクロロプロパノールのアルカリ水中への溶解度の低下により実用的な時間で予備反応が完結し難く、場合によっては塔へのフィード組成が不安定になる等の弊害が生じ、好ましくない。

本発明方法に使用される予備反応のための装置としては撹拌槽型反応器や管型反応器が挙げられる。後者の場合には反応器の一部を環状にして反応混合物が循環できるようにし、ポンプで液を循環して混合効果を高めることができる。循環路中に静的ミキサーを挿入してさらに混合効果を高めることもできる。また予備反応は連続式で行ってもよいし、回分式で行ってもよい。

本発明方法に使用される反応蒸留塔としては、充填塔，多孔板塔，ダウンカマー付多孔板塔等が挙げられるが、就中ダウンカマーを有する多孔板塔が最適である。例えば塔の最上段に還流液のフィード口、最上段より4～6段下方の段に原料ジクロロプロパノールとアルカリ分のためのフィード口、最下段の下に水蒸気吹込みノズルを設けたものが用いられる。

ジクロロプロパノールの転化率，エピクロルヒドリンの選択率共に90%以上得たいときは、理論段数は、本発明の予備反応を実施しない場合、通常13～17段が必要であるが、本発明方法によれば10～11段で十分である。

〔実施例〕

以下実施例により本発明のエピクロルヒドリンの製造方法をより具体的に説明する。なお例中組成%はいずれも重量単位であり、

転化率

$$= \left\{ 1 - \frac{\text{留出液中のジクロロプロパノールのモル数}}{\text{供給液中のジクロロプロパノールのモル数}} \right\} \times 100$$

選択率

$$= \frac{(\text{留出エピクロルヒドリンのモル数}) \times 100}{(\text{供給ジクロロプロパノールのモル数}) \times \text{転化率}} \times 100$$

である。

反応蒸留塔は、実験のため分解・組立てが容易にできるように製作した。塔本体は深さ15mmのダウンカマー付多孔板（開孔率13%）2枚を1組として両端フランジ付の内径100mmの鉄製円筒を1つのユニットとして所要段数に応じて該ユニットの数を増減できるようになっており、組立て後の段間隔は150mmである。原料及びアルカリ分のフィード口は上から5段目に、また最下段の下側に水蒸気吹込みノズルを設けた。塔頂抜出し口は伝熱面積0.3m²の套管式分縮器を経て伝熱面積0.3m²の套管式全縮器に接続されている。分縮器の凝縮液は原料フィード口と同じ段に、また全縮器の凝縮液は分液槽に入るように配管されている。分液槽の上層（水性層）は塔最上段に還流するように配管されており、下層（油層）は留出液受槽に入るようになっている。塔底からは液面調節計により液面を一定に保ちながら液が抜出され、缶出液受槽に入るように配管されている。全縮器出口及び分液槽上部は真空ポンプに接続し、塔の操作圧力を変えられるようにした。

実施例1

予備反応：

水5.9kg及び水酸化カルシウム5%を含有する懸濁液18.3kgを、それぞれ予め約40℃に予熱後、ジャケット付鉄製で容量50ℓの撹拌槽に仕込み、混合液を40℃で25分間予備反応を行った後、直ちに冷却し、10℃を超えない温度に保った。予備反応率は23%であった。

反応蒸留：

予備反応後の液を、上記撹拌槽の底部抜出口から、撹拌しながら2.54kg／hrで抜出し、上記と同濃度のアルカリ懸濁液4.86kg／hrと共に、上記反応蒸留塔に供給した。この反応蒸留塔は段数24段とし、水蒸気吹込みノズルから水蒸気1.7kg／hrを吹込み、塔頂圧力500mmHg，塔頂温度86℃，塔底温度99℃，分縮器温度82℃で8時間運転して塔を安定化させた。分縮率は塔頂留出物に対して40%であった。塔の安定化後、全縮器の凝縮液から分縮された油層をサンプリングし、ガスクロマトクロマトグラ

フ法で分析したところ、2,3－ジクロロ－1－プロパノールの転化率98.0％、エピクロルヒドリンの選択率98.5％、油層中の2,3－ジクロロ－1－プロパノールの含有量は3.9％であった。

実施例2

予備反応：

2,3－ジクロロ－1－プロパノール58.5％，1,3－ジクロロ－2－プロパノール4.4％，水26.9％，塩化水素10.2％の混合物17.6kgと水酸化カルシウム10％を含有する懸濁液31.0kgを用いて実施例1と同様にして60分間予備反応させた。予備反応率は40％であった。

反応蒸留：

実施例1と同様にして、予備反応を施した液4.86kg／hrと上と同濃度のアルカリ懸濁液2.54kg／hrを実施例1で用いたのと同じ反応蒸留塔に供給し、水蒸気吹込みノズルから水蒸気1.7kg／hrを吹込みつつ、塔頂圧力500mmHg，塔頂温度85℃，塔底温度99℃，分縮器温度80℃で8時間運転して塔を安定化させた。分縮率は塔頂留出物に対して50％であった。塔の安定化後、実施例1と同様にして生成物を分析したところ、2,3－ジクロロ－1－プロパノール及び1,3－ジクロロ－2－プロパノールの転化率は両者あわせて99.2％、エピクロルヒドリンの選択率98.3％、油層中の2,3－ジクロロ－1－プロパノール及び1,3－ジクロロ－2－プロパノールの含有量はそれぞれ1.1％及び0.1％であった。

比較例

実施例1において、予備反応を行わず、2,3－ジクロロ－1－プロパノール，水及び水酸化カルシウム懸濁液を、上記反応蒸留塔に直接供給し、実施例1と同様にして脱塩化水素反応を行った。2,3－ジクロロ－1－プロパノールの転化率は96.1％、エピクロルヒドリンの選択率は97.5％、油層中の2,3－ジクロロ－1－プロパノールの含有量は4.3％であった。

以上の実施例，比較例より、予備反応を行うことにより、ジクロロプロパノールの転化率と特にエピクロルヒドリンの選択率が改善されることは明らかである。

〔発明の効果〕

本発明の方法により予めジクロロプロパノールを過少のアルカリ分と低温で予備反応させた後、反応蒸留塔に供給することにより、不要な副反応を最小限に抑えることができる。その分、塔へ供給すべきアルカリ分を少くすることができて、塔内のアルカリ濃度を全体として低くでき、エピクロルヒドリンの加水分解を軽減できる。これらはいずれもジクロロプロパノールの転化率を高くしつつ、エピクロルヒドリンの選択率を向上させるのに効果がある。本発明法は高濃度のジクロロプロパノールを用いる場合、特に2,3－ジクロロ－1－プロパノールの見掛けの反応速度の低下が著しいので、その低下を補う方法として有効である。また2,3－ジクロロ－1－プロパノールと1,3－ジクロロ－2－プロパノールとの混合物を用いる場合、後者の反応速度の方が大きいので、予備反応を行うことにより後者が先に消費され、塔に供給されるときは前者の含量が相対的に多くなるので、塔内では前者に最適又はそれに近い操作条件を選択することができ、反応制御が容易になる。さらに反応が進んだ分だけ塔の段数を少くすることができ、全量塔内で反応させた場合よりも副生物を低減できるため缶出液中の有機物含量も少くすることができる等工業的に有用である。

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THE RESULTS OF EXAMINATION

☐ Rejected Claims: Claims 1-4, 18, 22, 27, and 32
☐ Rejected Items other than claims: none
☐ Allowable Claims: Claims 5-17, 19-21, 23-26, 28-31, 33, and 34

[Remark] Please note that another preliminary rejection may be issued after undergoing reexamination, if new rejection grounds are found in the application, including the claims and specification. In addition, the present application cannot be allowed until the rejection grounds set forth below are overcome.

THE EXAMINER'S GROUNDS FOR REJECTION

1. The present application cannot be allowed under Article 29(1)(ii) of the Patent Act because the inventions of Claims 1-4 lack novelty, as set forth below:

The subject matter in Claims 1-4 is described as the gist thereof. However, Japanese Patent Laid-Open Publication No. (Hei)03-223267 (published on October 2, 1991, hereinafter "cited reference"), which was published before the priority date of the present application, discloses the technology of producing epoxy resins wherein epichlorohydrin is produced via 2,3-dichloro-1-propanol and/or 1,3-dichloro-2-propanol and the same is used in the production of the epoxy resins. Upon comparing said claims with the cited reference, the technologies of Claims 1, 3, and 4, i.e., a process for producing epoxy resins wherein dichloropropanol containing 1,3-dichloropropane-2-ol is used as the starting material and that of Claim 2, i.e., a process for producing epoxy resins wherein dichloropropanol starting material is a mixture of isomers consisting of 1,3-dichloropropane-2-ol and 2,3-dichloropropane-1-ol, are identical to those of the cited reference. In addition, the concrete content of 1,3-dichloropropane-2-ol defined in Claims 1-4 is nothing more than a mere selection made by a person skilled in the art. Further, said definition does not foster any particular difference in the objective and effect of the invention.

2. The present application cannot be allowed because Claims 3, 18, 22, 27, and 32 fail to meet the description requirements under Article 42(4)(ii) of the Patent Act, as set forth below:

A. Claims 3 and 27 include the expressions, "preferably" and "besides," respectively, which render the invention unclear. In addition, Claim 18 describes "a process..., in which continuous or periodic withdrawal of a fraction comprising at least water with a hydrogen chloride content equal to or less than 10% by weight relative to the total weight of the fraction comprising water and optionally dichloropropanol is carried out, and the reaction medium is optionally fed with water, in particular steam." However, the expressions, such as "optionally," "equal to or less than," and "in particular," along with the unclear context make the invention